Photoswitchable and valence-free plasmonic superstructures by depletion-induced self-assembly

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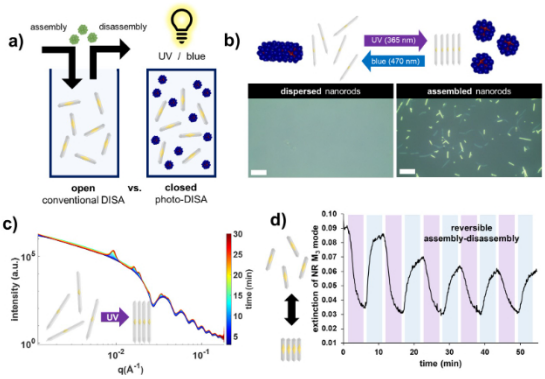
The depletion interaction is a chemically-universal (valence-free) attractive force observed in many colloidal systems, and is important in water treatment, biomolecular interactions, and the self-assembly of nanoparticles. While using depletants is useful for controlling the stabilization of mixtures and assemblies, this interaction requires external addition of material into an open system. Active metamaterials are stimuli-responsive systems with opto-electronic properties not found in nature. We recently reported a method for preparing such reconfigurable superstructures via depletion-induced self-assembly (DISA) of plasmonic nanorods (NRs) using CTAC micelles as depletants [1-2]. While DISA is promising, switching between the assembled and disassembled states currently requires redilution, making it impractical. To overcome this "open system" limitation, we propose using azobenzene-based photosurfactant micelles as light-sensitive depletants (photo-DISA) to have in situ switchable superstructures in a "closed system".

Our system consists of passive silver nanorods dispersed in water together with active AzoTAB photosurfactant. Although photosurfactants are well known [3], their use as photoswitchable depletants is proposed here for the first time. AzoTAB micelles change their size and shape depending on their isomerization state, thus modulating the attractive depletion force acting on the NRs [Fig. 1a-b]. By irradiating a nanorod/AzoTAB suspension with UV or blue light, we can reversibly switch between assembled and disassembled NR states with a full cycle time of 2-3 min. Switching between UV and blue irradiation also tunes the inter-NR gap in the assemblies. This 're-contractable' system yields tunable plasmonic enhancement which modulates the detected Raman (SERS) signal of analytes like methylene blue [Fig. 1c-d].

This work offers a new strategy of creating active, light-sensitive, plasmonic metamaterials via photo-DISA, which can be extended to a wide range of nanostructures with different composition or surface chemistry due to the universal nature of depletion. Finally, our photo-DISA system serves as a potential platform for tunable and switchable plasmonic detection via SERS.



a) Open DISA versus closed photo-DISA. b) Reversible photoswitchable assembly of silver nanorods into plasmonic superstructures with AzoTAB. c) SAXS kinetics of photo-DISA. d) Cyclic NR assembly-disassembly by alternate UV/blue irradiation. Scale bars are 10 µm.

References:

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